

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 February 2001 (22.02.2001)

PCT

(10) International Publication Number
WO 01/11957 A1

- (51) International Patent Classification⁷: A01N 25/30, 57/20, C11D 1/44, C08G 65/00
- (21) International Application Number: PCT/US00/22542
- (22) International Filing Date: 17 August 2000 (17.08.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/149,573 18 August 1999 (18.08.1999) US
60/149,541 18 August 1999 (18.08.1999) US
- (71) Applicant: HUNTSMAN PETROCHEMICAL CORPORATION [US/US]; 7114 North Lamar Boulevard, Austin, TX 78752 (US).
- (72) Inventors: ASHRAWI, Samir, S.; 13228 Darwin Lane, Austin, TX 78729-7499 (US). STRIDDE, Howard, Meyer; 304 Norwood Drive, Georgetown, TX 78628-8364 (US).
- (74) Agents: HEADLEY, Tim et al.; Haynes and Boone, L.L.P., Suite 4300, 1000 Louisiana Street, Houston, TX 77002-5012 (US).
- (81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— With international search report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 01/11957 A1

(54) Title: POLYETHER DIAMINE-BASED SURFACTANT ADJUVANTS AND COMPOSITIONS THEREOF

(57) Abstract: Surfactants that are expected to further improve the bioefficacy of herbicides. The surfactants comprise esterified alkoxylated polyether diamines, alkoxylated polyether diamines, and mixtures thereof. The present invention also provides for herbicide compositions that contain the surfactants of the present invention. The herbicide compositions comprise a herbicidal active ingredient, a surfactant of the present invention, and optionally, one or more formulation aids. The present invention additionally provides for a method of controlling unwanted weeds or vegetation using the herbicide compositions of the present invention.

POLYETHER DIAMINE - BASED SURFACTANT ADJUVANTS AND COMPOSITIONS THEREOF

Technical Field

5 This invention relates to surfactants, and, more particularly, to surfactants that enhance the bioefficacy of herbicides, and to herbicide compositions comprising such surfactants.

Background of the Invention

 Herbicide compositions are often characterized according to the identity
10 of the active ingredient, and by the mode by which the active ingredient causes vegetation necrosis. Regardless of the active ingredient, most herbicides cause vegetation necrosis by interfering with one or more vital biological processes essential to the vegetation's survival. Yet, before the active ingredient of a herbicide can interfere with such biological processes, the active ingredient
15 must somehow be absorbed into the vegetation. Unfortunately, this absorption is often hindered by the chemical nature of the active ingredient.

 Accordingly, in addition to active ingredients, most herbicide compositions also comprise other components, commonly termed adjuvants, that enhance the performance and absorption of the active ingredient. One
20 class of adjuvants that is frequently used is surfactants. Surfactants are useful in herbicide compositions because they tend to both enhance the absorbing properties of the active ingredient, as well as facilitate application of the herbicide.

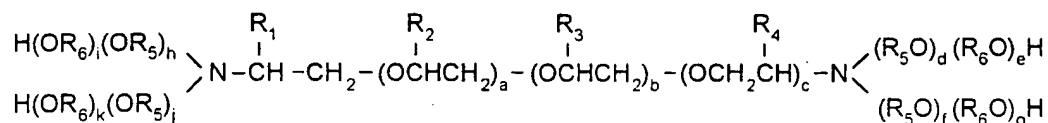
 The literature discloses various classes of surfactants, including
25 alkoxylated diamines. However, the literature appears to lack any reference to the use of alkoxylated polyether diamines or esterified alkoxylated polyether diamines as suitable herbicide adjuvants. It is expected that both alkoxylated polyether diamines and esterified alkoxylated polyether diamines will function to improve the bioefficacy of herbicide compositions containing such
30 surfactants. Accordingly, the present invention is directed toward surfactant adjuvants that include alkoxylated polyether diamines, esterified alkoxylated polyether diamines, and mixtures thereof, herbicide compositions comprising

such surfactant adjuvants, and a method of controlling unwanted vegetation using such herbicide compositions.

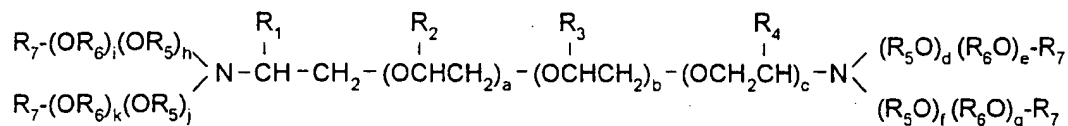
Summary of the Invention

The present invention provides for surfactants that are expected to further improve the bioefficacy of herbicides. The surfactants comprise alkoxyated polyether diamines (I), esterified alkoxyated polyether diamines (IIa) or (IIb), or mixtures thereof, with the following general structure:

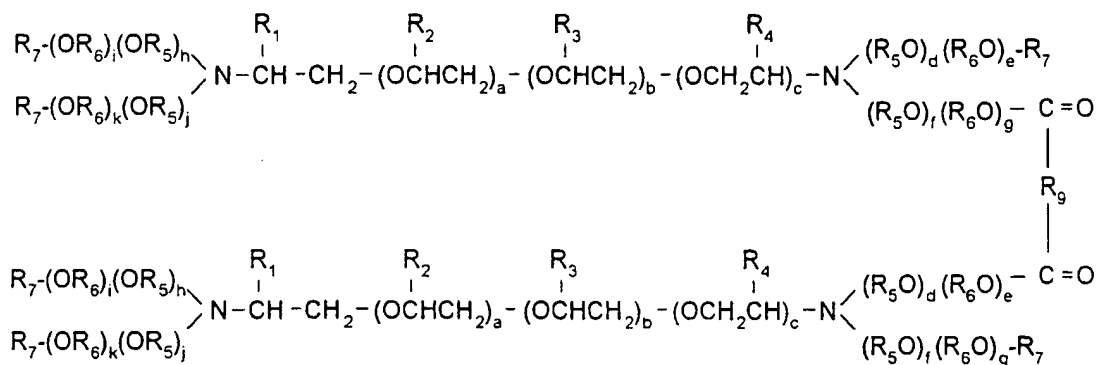
(I)



10 (IIa)

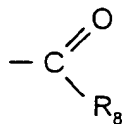


(IIb)



where R_1 , R_2 , R_3 , and R_4 are each independently hydrogen, CH_3 , or CH_2CH_3 ; a , b , and c each vary from zero to about forty; R_5 and R_6 are each independently a straight or branched chain alkenyl group with from about two to about six

carbon atoms; d, e, f, g, h, i, j, and k each vary from zero to about twenty-two; each R_7 is independently either a hydrogen or has the following general structure:



where each R_8 is independently a linear or branched alkyl or alkenyl with less than about twenty-two carbon atoms; and, R_9 is an alkyl or alkenyl with less than about twenty-two carbon atoms.

The present invention also provides for herbicide compositions that contain a surfactant of the present invention. The herbicide compositions comprise a herbicidal active ingredient, a surfactant of the present invention, and optionally, one or more formulation aids. The herbicide compositions of the present invention are expected to have a reduced tendency to cause eye and skin irritation.

The present invention additionally provides for a method of controlling unwanted weeds or vegetation using the herbicide compositions of the present invention.

Detailed Description of the Preferred Embodiment

The present invention relates to surfactants that are expected to enhance the bioefficacy of herbicides, herbicide compositions comprising such surfactants, and a method of controlling unwanted weeds or vegetation using the herbicide compositions of the present invention. The surfactants of the present invention are expected to enhance the bioefficacy of herbicides because they have twice the amine content as traditional herbicide surfactants (*i.e.* tallowamine ethoxylates). This increased amine content will likely enhance the ability of the herbicide to penetrate the tissue of the vegetation, thereby increasing the bioefficacy of the herbicide. In addition, the surfactants of the present invention are expected to have improved handling characteristics, including a lower volatility, due to the polyether "interior" structure of the surfactants. Further, when added to glyphosate solutions, the surfactants of

the present invention produce cloud points at or above about 65°C, the commercial standard for glyphosate herbicide solutions.

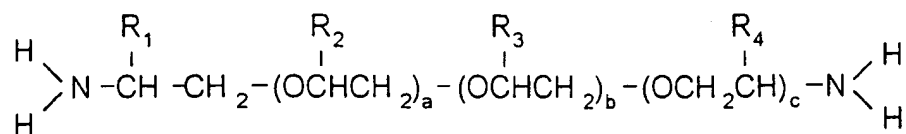
The surfactants of the present invention may be used in conjunction with any number of herbicidal active ingredients, including, but not limited to, various salts of glyphosate and gluphosinate. However, the use of the surfactants of the present invention with glyphosate is of particular interest because glyphosate is probably the most widely used herbicide.

Glyphosate, or N-phosphonomethylglycine, is a broad-spectrum herbicide that is useful on essentially all annual and perennial plants, including, grasses, broad-leaved weeds, and woody plants. Glyphosate promotes plant necrosis by inhibiting aromatic amino acid biosynthesis. By inhibiting aromatic amino acid synthesis, and thereby protein synthesis, glyphosate initially suppresses plant growth, which is soon followed by plant necrosis.

In its free acid form, glyphosate has a low water solubility. As such, water-based glyphosate compositions typically contain a water soluble salt of glyphosate, such as the isopropylamine salt. For example, many commercially available herbicide compositions contain the water soluble mono-isopropylamine salt of glyphosate. Glyphosate, and various water soluble derivatives of glyphosate are available from numerous manufactures.

The surfactants of the present invention may be prepared by reacting a polyether diamine with one or more lower molecular weight alkylene oxides, at a temperature from about 100°C to about 110°C, at a pressure of about 60 psig, and in the presence of a suitable alkaline catalyst. The polyether diamines may be alkoxyated to varying degrees. Preferably, the resulting polyether diamines have an alkylene oxide content less than about 90 percent.

The polyether diamine used to make the alkoxyated polyether diamine surfactants of the present invention should have the following general structure:

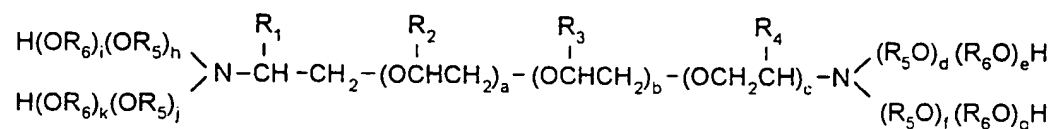


where R_1 , R_2 , R_3 , and R_4 are each independently hydrogen, CH_3 , or CH_2CH_3 ; and a , b , and c each vary from zero to about forty. Preferably, the polyether diamine comprises a JEFFAMINE® diamine (commercially available from the Huntsman Corporation, Houston, Texas).

5 The lower molecular weight alkylene oxide may comprise one or more alkylene oxides with less than about six carbon atoms. Preferably, the alkylene oxide comprises ethylene oxide, propylene oxide, butylene oxide, or mixtures thereof.

Any suitable alkoxylation catalyst may be used in the alkoxylation
10 process. Preferably, the catalysts comprises a 45% aqueous solution of potassium hydroxide.

The resulting alkoxyated polyether diamine surfactants of the present invention have the following general structure:



15 where R_1 , R_2 , R_3 , and R_4 are each independently hydrogen, CH_3 , or CH_2CH_3 ; a , b , and c each vary from zero to about forty; R_5 and R_6 are each independently a straight or branched chain alkenyl group with from about two to about six carbon atoms; and d , e , f , g , h , i , j , and k each vary from zero to about twenty-two.

After preparation, the resulting alkoxyated polyether diamine
20 surfactants of the present invention may then be blended with one or more formulation aids before being combined with a herbicide. Such formulation aids may include neutralizing agents, water, anti-freeze agents, or mixtures thereof. The neutralizing agents may include, but are not limited to, hydrochloric acid or sulfuric acid, carboxylic acids with less than about twenty
25 carbon atoms, sulfonic acids, acid sulfates, acid phosphate esters, and/or acid carboxylates. A sufficient amount of a neutralizing agent should be added to the surfactant to neutralize any residual basicity (*i.e.* to achieve a pH of about

7.0). The anti-freeze agents may include, but are not limited to ethylene glycol, diethylene glycol, propylene glycol, and polyethylene glycols.

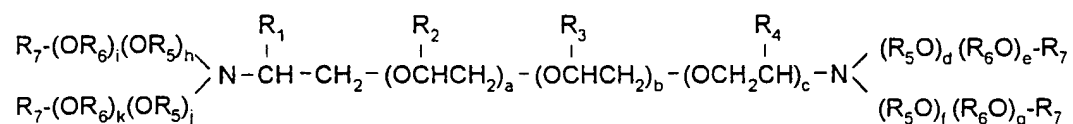
The relative amount of formulation aids that should be blended with the alkoxyated polyether diamine surfactants of the present invention will
 5 depend on a variety of factors, including the nature of the herbicide to be blended with the surfactant solution, the proposed mode of application of the final herbicide formulation, the nature of the vegetation to be treated, etc.

Alternatively, the alkoxyated polyether diamines may be esterified by reacting the alkoxyated polyether diamines with one or more carboxylic acids.
 10 The esterification reaction should take place at a temperature from about 190°C to about 210°C, in an esterification vessel, with agitation, under nitrogen, and in the presence of an acid catalyst. The esterification reaction should proceed until all the water produced by the esterification reaction has been collected.

15 The carboxylic acid may include, but is not limited to, alkyl, alkylene, aryl, alkylaryl monocarboxylic acids or dicarboxylic acids with less than about twenty-two carbon atoms, carboxylic acids based on non-ionic surfactants formed from the reaction of a OH-containing hydrophobe and various alkylene oxides (ether carboxylates), or mixtures thereof. Preferably, the carboxylic
 20 acid comprises a tall oil fatty acid.

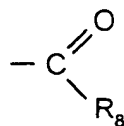
The catalyst may comprise any suitable esterification catalyst. Preferably, the acid catalyst comprises *p*-toluenesulfonic acid.

If the alkoxyated polyether diamines are esterified with a monocarboxylic acid(s), the resulting esterified alkoxyated polyether diamines
 25 have the following general structure:



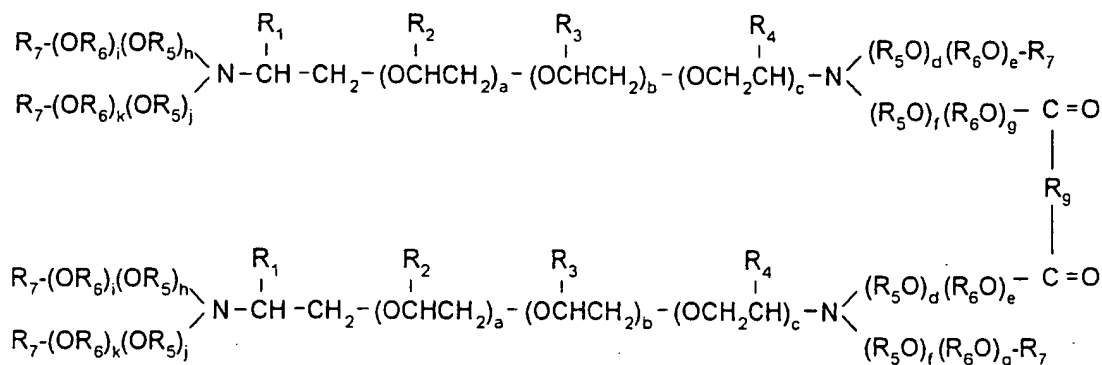
where R_1 , R_2 , R_3 , and R_4 are each independently hydrogen, CH_3 , or CH_2CH_3 ; a , b , and c each vary from zero to about forty; R_5 and R_6 are each independently a straight or branched chain alkenyl group with from about two to about six

carbon atoms; d, e, f, g, h, i, j, and k each vary from zero to about twenty-two; and each R₇ is independently either a hydrogen or has the following general structure:

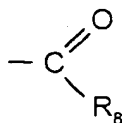


where each R₈ is independently a linear or branched alkyl or alkenyl with less
5 than about twenty-two carbon atoms.

If the alkoxyated polyether diamines are esterified with a dicarboxylic acid, or a dicarboxylic acid and a monocarboxylic acid(s), the resulting esterified alkoxyated polyether diamines have the following general structure:



10 where R₁, R₂, R₃, and R₄ are each independently hydrogen, CH₃, or CH₂CH₃; a,
b, and c each vary from zero to about forty; R₅ and R₆ are each independently a
straight or branched chain alkenyl group with from about two to about six
carbon atoms; d, e, f, g, h, i, j, and k each vary from zero to about twenty-two;
each R₇ is independently either a hydrogen or has the following general
15 structure:



where each R_8 is independently a linear or branched alkyl or alkenyl with less than about twenty-two carbon atoms; and, R_9 is an alkyl or alkenyl with less than about twenty-two carbon atoms.

5 The resulting esterified alkoxyated polyether diamine surfactants of the present invention may then be blended with one or more formulation aids before being combined with a herbicide. Such formulation aids may include neutralizing agents, water, anti-freeze agents, or mixtures thereof. The neutralizing agents may include, but are not limited to, hydrochloric acid or sulfuric acid. A sufficient amount of a neutralizing agent should be added to
10 the surfactant to neutralize any residual basicity (*i.e* to achieve a pH of about 7.0). The anti-freeze agents may include, but are not limited to ethylene glycol, diethylene glycol, propylene glycol, and polyethylene glycols.

The relative amount of formulation aids that should be blended with the esterified alkoxyated polyether diamine surfactants of the present
15 invention will depend on a variety of factors, including the nature of the herbicide to be blended with the surfactant solution, the proposed mode of application of the final herbicide formulation, the nature of the vegetation to be treated, etc.

After preparation, the alkoxyated polyether diamine and esterified
20 alkoxyated polyether diamine surfactant compositions of the present invention, or mixtures thereof, may then be blended with a herbicide. The relative amount of the alkoxyated polyether diamine and/or esterified alkoxyated polyether diamine surfactant compositions of the present invention that should be blended with a herbicide will vary depending on a
25 variety of factors, including the nature of the herbicide, the nature of the vegetation to be treated, the method of application, whether the herbicide is a water-based or a granular formulation, etc. In any case, the resulting herbicide compositions of the present invention should include a herbicidally effective amount of a herbicidal active ingredient, and a sufficient amount of a
30 surfactant composition of the present invention to enhance the effectiveness of the herbicidal active ingredient. The term "herbicidally effective amount" means the amount of herbicide necessary to promote plant necrosis. The

term "surfactant composition" means the surfactants of the present invention blended with one or more formulation aids.

The herbicide compositions of the present invention may be prepared as either liquid or solid compositions. Liquid compositions may include solutions
5 ready for immediate application, aqueous concentrates intended to be diluted with water before application, or microencapsulated actives suspended in liquid media. Solid compositions may include, but are not limited to, water dispersible granules, water soluble granules, microencapsulated actives, free-flowing particulate compositions, or granular-based solids that have been
10 compressed into tablets or briquets of any desired size and shape. Optionally, solid compositions may include formulations where the herbicide composition is absorbed onto water soluble or water insoluble inert dry carriers, including, but not limited to, Magnesol® (commercially available from the Dallas Group of America, Inc., Whitehouse, New Jersey).

15 Accordingly, the herbicide compositions of the present invention may be applied to vegetation as either a liquid or solid composition. Liquid herbicide compositions are typically sprayed on the vegetation to be treated, and typically comprise either liquid concentrates or dissolved or dispersed solid compositions. Liquid compositions may also be injected into, or painted on the
20 truck portion of the vegetation to be treated. Solid granular compositions may be spread on or around the vegetation to be treated.

Herbicide compositions comprising the alkoxylated polyether diamine and/or esterified alkoxylated polyether diamine surfactant compositions of the present invention are expected to have a reduced tendency to cause eye
25 irritation. Reduced eye irritation is expected because the pH of the alkoxylated polyether diamine and esterified alkoxylated polyether diamine surfactant compositions of the present invention is about 7.0. Because herbicide formulations are often applied by humans, or in locales with humans or animals, reduced eye irritation is a desirable feature in such formulations.

30 It is understood that variations may be made in the foregoing with departing from the scope of the invention. For example, although the surfactants of the present invention are primarily discussed as being

incorporated into water-based herbicide compositions, it is understood that the surfactants of the present invention may also be incorporated into dry granular herbicide formulations. In addition, although the surfactants of the present invention are primarily discussed as being incorporated into
5 glyphosate solutions, the surfactants of the present invention may be incorporated into any number of other herbicide formulations, including, but not limited to, macro and micro emulsions, suspensions, suspension concentrates, and other liquid and solid formulations known to those skilled in the art, to increase the bioefficacy of such herbicides.

10 The following examples are illustrative of the present invention, and are not intended to limit the scope of the invention in any way.

Preparation of the Alkoxylated Polyether Diamines

Example 1

20 pounds of JEFFAMINE® XTJ-511 were charged to a nitrogen
15 purged reactor. The reactor pressure was then increased to 60 psig, and vented down to 0 three times. The reactor was then purged with nitrogen, at a temperature of about 115 °C, until the weight percent of water was reduced to less than .05%. The JEFFAMINE® XTJ-511 was then reacted with ethylene oxide to produce a product with varying degrees of ethylene oxide
20 content. The ethoxylation was conducted at a temperature from about 100°C to about 110°C, at a pressure of about 60 psig, and in the presence of a 45% aqueous potassium hydroxide solution.

Preparation of a Surfactant Solution Containing the

Alkoxylated Polyether Diamine

25

Example 2

The alkoxylated polyether diamine produced in Example 1 (with a 10% ethylene oxide content) was then blended to achieve a pH neutral solution, as follows:

	<u>Component</u>	<u>Amount</u>
	Alkoxylated polyether diamine w/ a 10% EO content produced in Example 1	73%
	Concentrated HCl	20%
5	Water	7%

Bioefficacy Testing of Glyphosate Solutions Containing the Alkoxylated Polyether Diamine Surfactants of the Present Invention

Example 3 (Prophetic)

The surfactant solution prepared in Example 2 is then blended with a
 10 glyphosate solution. Rodeo® is used as the source of glyphosate. (Rodeo® contains 648 g/L of the mono-isopropylamine salt of glyphosate.) The glyphosate solution is then sprayed on a variety of weeds. The weeds are examined approximately twenty-one days after treatment with the glyphosate solution containing a surfactant of the present invention. The weeds appear
 15 to be significantly affected by the treatment, and most appear to be dead.

Preparation of the Esterified Alkoxylated Polyether Diamines

Example 4

4.7 pounds of JEFFAMINE® XTJ-511 were charged to a nitrogen purged reactor. The reactor pressure was then increased to 60 psig, and
 20 vented down to 0 three times. The reactor was then purged with nitrogen, at a temperature of about 115 °C, until the weight percent of water was reduced to less than .05%. The JEFFAMINE® XTJ-511 was then reacted with ethylene oxide to produce a product with about a 30% ethylene oxide content. The reaction was conducted at a temperature from about 100°C to about
 25 110°C, at a pressure of about 60 psig, and in the presence of a 45% aqueous potassium hydroxide solution.

850.3 grams of the alkoxylated polyether diamine prepared above and 149.7 grams of a tall oil fatty acid were charged to a three-necked flask. The reaction components were then heated to a temperature from about 190°C to
 30 about 210°C, with agitation, under nitrogen sparge and vacuum. Then,

approximately 1 percent of *p*-toluenesulfonic acid was added, and the esterification reaction was continued until the calculated water of esterification had been collected.

Preparation of a Surfactant Solution Containing the Esterified Alkoxyated Polyether Diamine

Example 5

The esterified alkoxyated polyether diamine produced in Example 4 was then blended to achieve a pH neutral solution, as follows:

	<u>Component</u>	<u>Amount</u>
10	Esterified alkoxyated polyether diamine produced in Example 4	78.4%
	Concentrated HCl	4.6%
	Water	17.0%

Bioefficacy Testing of Glyphosate Solutions Containing the Esterified Alkoxyated Polyether Diamine Surfactants of the Present Invention

Example 6 (Prophetic)

The surfactant solution prepared in Example 5 is then blended with a glyphosate solution. Rodeo® is used as the source of glyphosate. (Rodeo® contains 648 g/L of the mono-isopropylamine salt of glyphosate.) The glyphosate solution is then sprayed on a variety of weeds. The weeds are examined approximately twenty-one days after treatment with the glyphosate solution containing a surfactant of the present invention. The weeds appear to be significantly affected by the treatment, and most appear to be dead.

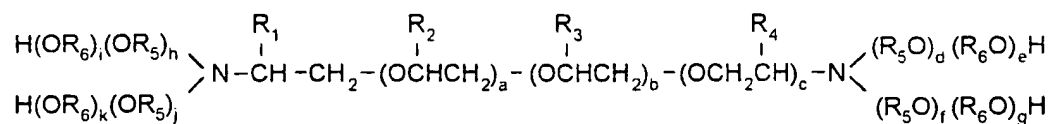
Although illustrative embodiments have been shown and described, a wide range of modification, changes, and substitution is contemplated in the foregoing disclosure. In some instances, some features of the disclosed embodiments may be employed without a corresponding use of the other

features. Accordingly, it is appropriate that the appended claims be construed broadly and in a manner consistent with the scope of the invention.

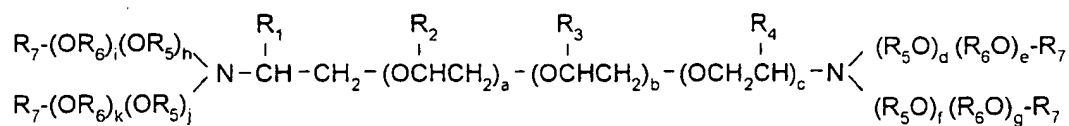
Claims

- 1 1. A herbicide composition that comprises:
 2 a. a herbicidally effective amount of a herbicidal active ingredient;
 3 and
 4 b. a sufficient amount of a surfactant component that enhances the
 5 effectiveness of the herbicidal active ingredient, wherein the
 6 surfactant component comprises either alkoxyated polyether
 7 diamines (I), esterified alkoxyated polyether diamines (IIa) or
 8 (IIb), or mixtures thereof, with the following general structure:

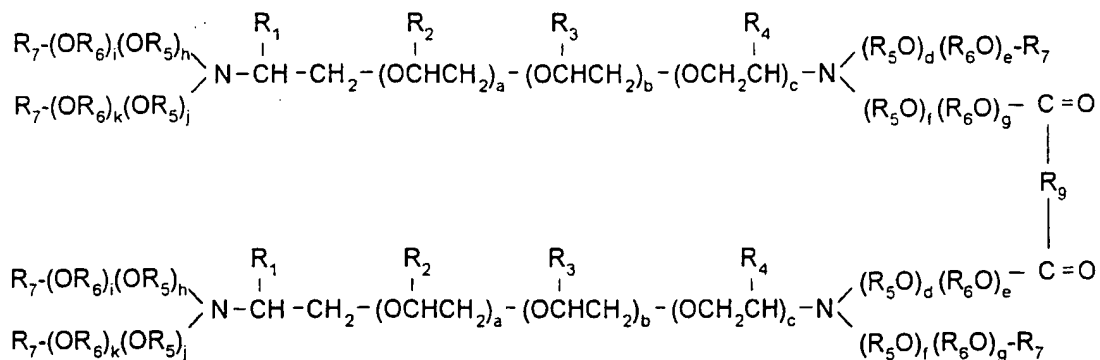
(I)



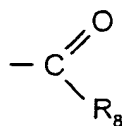
(IIa)



(IIb)



9 where R_1 , R_2 , R_3 , and R_4 are each independently hydrogen, CH_3 , or
 10 CH_2CH_3 ; a, b, and c each vary from zero to about forty; R_5 and R_6 are
 11 each independently a straight or branched chain alkenyl group with
 12 from about two to about six carbon atoms; d, e, f, g, h, i, j, and k each
 13 vary from zero to about twenty-two; each R_7 is independently either a
 14 hydrogen or has the following general structure:



15
 16 where each R_8 is independently a linear or branched alkyl or alkenyl with less
 17 than about twenty-two carbon atoms; and, R_9 is an alkyl or alkenyl with less
 18 than about twenty-two carbon atoms.

1 2. The composition of claim 1, wherein the herbicidal active ingredient
 2 comprises glyphosate or a salt thereof.

1 3. The composition of claim 1, wherein R_5 and R_6 are each independently a
 2 straight or branched chain alkenyl group with from about two to about
 3 four carbon atoms.

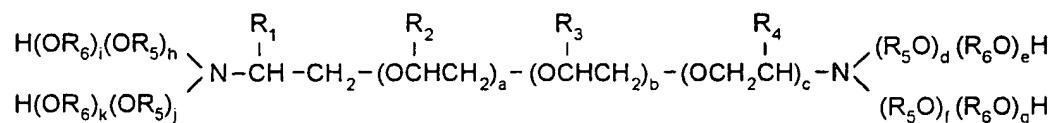
1 4. The composition of claim 1, wherein the surfactant component further
 2 comprises a formulation aid.

1 5. The composition of claim 4, wherein the formulation aid is selected
 2 from the group consisting of neutralizing agents, water, anti-freeze
 3 agents, and mixtures thereof.

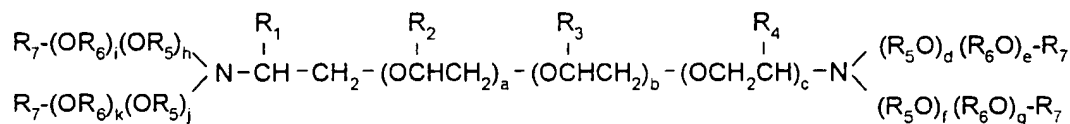
1 6. The composition of claim 5, wherein the neutralizing agent is selected
 2 from the group consisting of hydrochloric acid, sulfuric acid, carboxylic
 3 acids with less than about twenty carbon atoms, sulfonic acids, acid
 4 sulfates, acid phosphate esters, and acid carboxylates.

- 5 7. The composition of claim 4, wherein the composition has a reduced
6 tendency to cause eye irritation.
8. A herbicide composition that comprises:
- a herbicidally effective amount of glyphosate or a salt thereof;
and
 - a sufficient amount of a surfactant component that enhances the effectiveness of the herbicidal active ingredient, wherein the surfactant component comprises either alkoxyated polyether diamines (I), esterified alkoxyated polyether diamines (IIa) or (IIb), or mixtures thereof, with the following general structure:

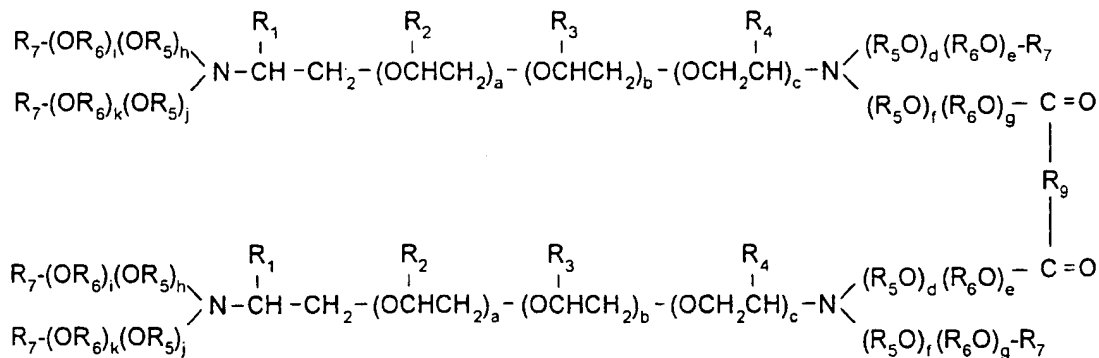
(I)



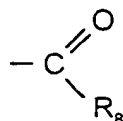
(IIa)



(IIb)



8 where R_1 , R_2 , R_3 , and R_4 are each independently hydrogen, CH_3 ,
 9 or CH_2CH_3 ; a, b, and c each vary from zero to about forty; R_5 and
 10 R_6 are each independently a straight or branched chain alkenyl
 11 group with from about two to about six carbon atoms; d, e, f, g, h,
 12 i, j, and k each vary from zero to about twenty-two; each R_7 is
 13 independently either a hydrogen or has the following general
 14 structure:



15 where each R_8 is independently a linear or branched alkyl or
 16 alkenyl with less than about twenty-two carbon atoms; and, R_9 is
 17 an alkyl or alkenyl with less than about twenty-two carbon
 18 atoms.

1 9. The composition of claim 8, wherein R_5 and R_6 are each independently a
 2 straight or branched chain alkenyl group with from about two to about
 3 four carbon atoms.

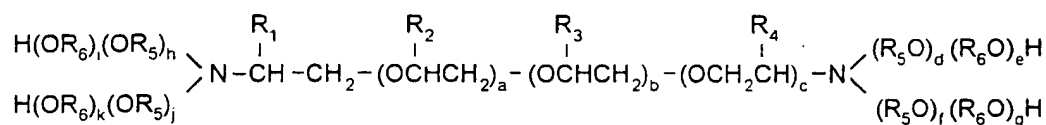
1 10. The composition of claim 8, wherein the surfactant component further
 2 comprises a formulation aid.

1 11. The composition of claim 10, wherein the formulation aid is selected
 2 from the group consisting of neutralizing agents, water, anti-freeze
 3 agents, and mixtures thereof.

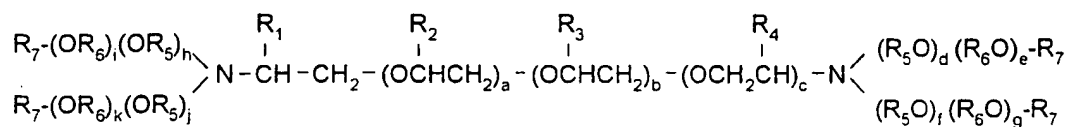
1 12. The composition of claim 11, wherein the neutralizing agent is selected
 2 from the group consisting of hydrochloric acid, sulfuric acid, carboxylic
 3 acids with less than about twenty carbon atoms, sulfonic acids, acid
 4 sulfates, acid phosphate esters, and acid carboxylates.

- 1 13. The composition of claim 10, wherein the composition has a reduced
2 tendency to cause eye irritation.
- 1 14. A surfactant for increasing the bioefficacy of a herbicide, wherein the
2 surfactant comprises either alkoxyated polyether diamines (I),
3 esterified alkoxyated polyether diamines (IIa) or (IIb), or mixtures
4 thereof, with the following general structure:

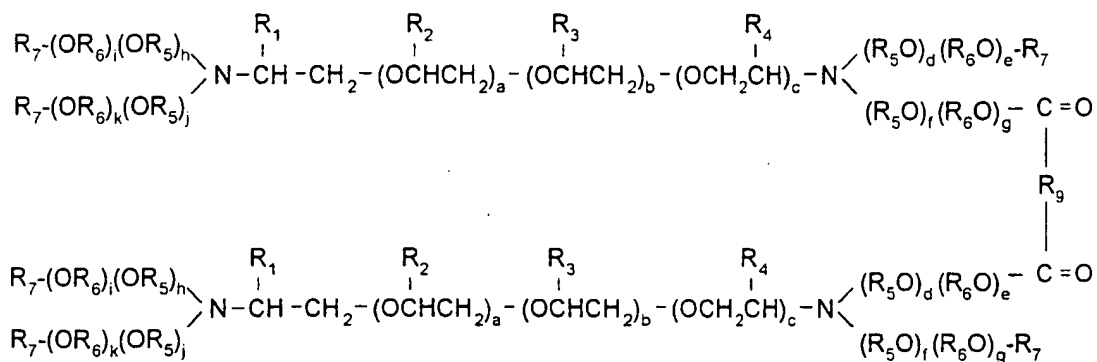
(I)



(IIa)

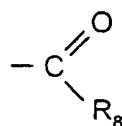


(IIb)



- 5 where R_1 , R_2 , R_3 , and R_4 are each independently hydrogen, CH_3 , or
6 CH_2CH_3 ; a, b, and c each vary from zero to about forty; R_5 and R_6 are
7 each independently a straight or branched chain alkenyl group with
8 from about two to about six carbon atoms; d, e, f, g, h, i, j, and k each

9 vary from zero to about twenty-two; each R_7 is independently either a
 10 hydrogen or has the following general structure:



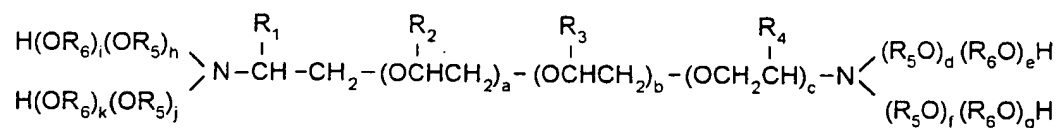
11 where each R_8 is independently a linear or branched alkyl or
 12 alkenyl with less than about twenty-two carbon atoms; and, R_9 is
 13 an alkyl or alkenyl with less than about twenty-two carbon
 14 atoms.

1 15. The surfactant of claim 14, wherein R_5 and R_6 are each independently a
 2 straight or branched chain alkenyl group with from about two to about
 3 four carbon atoms.

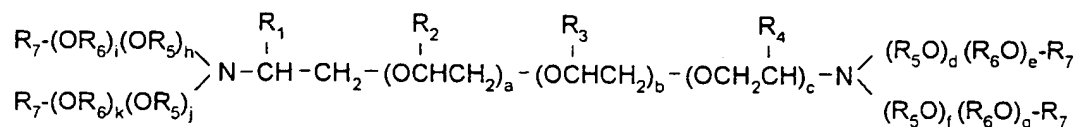
1 16. A surfactant composition for increasing the bioefficacy of a herbicide
 2 that comprises:

3 a. alkoxyated polyether diamines (I), esterified alkoxyated
 4 polyether diamines (IIa) or (IIb), or mixtures thereof, with the
 5 following general structure:

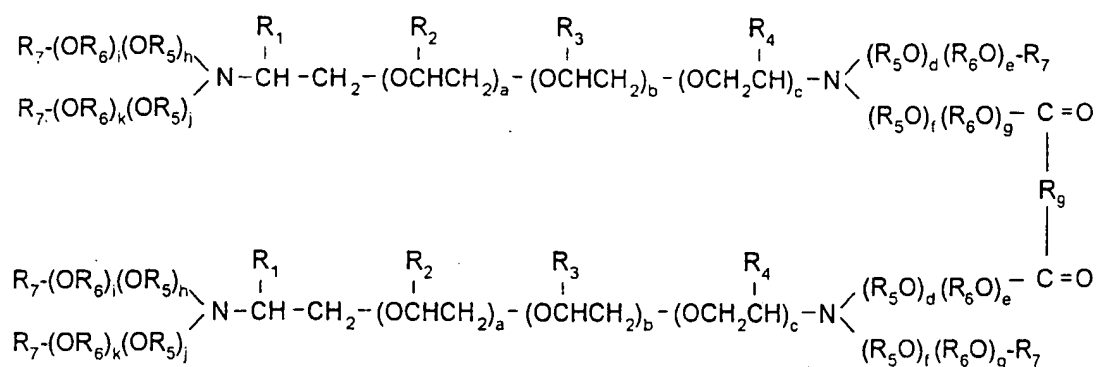
(I)



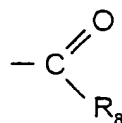
(IIa)



(IIb)



6 where R_1 , R_2 , R_3 , and R_4 are each independently hydrogen, CH_3 ,
 7 or CH_2CH_3 ; a , b , and c each vary from zero to about forty; R_5 and
 8 R_6 are each independently a straight or branched chain alkenyl
 9 group with from about two to about six carbon atoms; d , e , f , g , h ,
 10 i , j , and k each vary from zero to about twenty-two; each R_7 is
 11 independently either a hydrogen or has the following general
 12 structure:



13 where each R_8 is independently a linear or branched alkyl or
 14 alkenyl with less than about twenty-two carbon atoms; and, R_9 is
 15 an alkyl or alkenyl with less than about twenty-two carbon
 16 atoms; and

17 b. a formulation aid.

1 17. The composition of claim 16, wherein R_5 and R_6 are each independently
 2 a straight or branched chain alkenyl group with from about two to
 3 about four carbon atoms.

1 18. The composition of claim 16, wherein the formulation aid is selected
 2 from the group consisting of water, neutralizing agents, anti-freeze

- 3 agents, dyes, thickening agents, anti-foaming agents, UV stabilizers,
and mixtures thereof.
- 1 19. The composition of claim 18, wherein the neutralizing agent is selected
2 from the group consisting of hydrochloric acid, sulfuric acid, carboxylic
3 acids with less than about twenty carbon atoms, sulfonic acids, acid
4 sulfates, acid phosphate esters, and acid carboxylates.
- 1 20. The composition of claim 16, wherein the composition has a reduced
2 tendency to cause eye irritation when mixed with a herbicidal active
3 ingredient.
- 1 21. The composition of claim 16, wherein the composition has a cloud point
2 greater than about 65°C when mixed with a herbicidal active
3 ingredient.
- 1 22. A method of killing or controlling weeds or unwanted vegetation
2 comprising the step of applying a herbicidally effective amount of the
3 composition of claim 1 to the foliage or tissue of the weeds or unwanted
4 vegetation.
- 1 23. A method of killing or controlling weeds or unwanted vegetation
2 comprising the step of applying a herbicidally effective amount of the
3 composition of claim 8 to the foliage or tissue of the weeds or unwanted
4 vegetation.

INTERNATIONAL SEARCH REPORT

Intern. nal Application No

PCT/US 00/22542

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N25/30 A01N57/20 C11D1/44 C08G65/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 24313 A (GRIFFITHS PAUL LESLIE ;ICI AUSTRALIA OPERATIONS (AU); KIRBY ANDREW) 11 June 1998 (1998-06-11) page 1 -page 3, line 5 page 4, line 6 -page 6, line 16; claims ---	1-23
X	US 3 639 262 A (MILLIGAN JOHN G) 1 February 1972 (1972-02-01) column 1, line 11 - line 16 column 1, line 33 - line 39 column 1, line 54 - line 64 column 2, line 31 - line 36; claims 3-8 ---	1,3-7, 14-23
X	EP 0 862 857 A (OSI SPECIALTIES INC) 9 September 1998 (1998-09-09) page 2, line 1 - line 35; claims ---	1-23
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

24 November 2000

Date of mailing of the international search report

05/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Muellners, W

INTERNATIONAL SEARCH REPORT

Intern. Patent Application No

PCT/US 00/22542

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 05779 A (RHONE POULENC CHIMIE ; GUBELMANN ISABELLE (FR)) 20 February 1997 (1997-02-20) page 1, line 34 - page 2, line 19 page 3, line 1 - line 18 ----	1-23
X	EP 0 489 322 A (BASF AG) 10 June 1992 (1992-06-10) page 3, line 14 - line 22; claims 1,2 ----	14-19,21
X	US 3 309 182 A (R.P.CROWLEY) 14 March 1967 (1967-03-14) column 1, line 42 - line 68 ----	14-17,21
A	WYRILL J B ET AL: "GLYPHOSATE TOXICITY TO COMMON MILKWEED AND HEMP DOGBANE AS INFLUENCED BY SURFACTANTS" WEED SCIENCE, US, WEED SCIENCE SOCIETY OF AMERICA, CHAMPAIGN, IL, vol. 25, no. 3, 1 May 1977 (1977-05-01), pages 275-287, XP002034447 ISSN: 0043-1745 the whole document ----	1-23
A	EP 0 472 310 A (WITCO CORP) 26 February 1992 (1992-02-26) page 2, line 3 - line 36 page 2, line 57 - page 3, line 36 page 4, line 5 - line 28 ----	1-23
A	US 5 902 772 A (MAGIN RALPH W ET AL) 11 May 1999 (1999-05-11) column 1, line 16 - column 2, line 23 ----	1-23
A	DE 40 19 362 A (RHONE POULENC AGROCHIMIE) 3 January 1991 (1991-01-03) page 2, line 34 - line 54 -----	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/22542

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9824313 A	11-06-1998	AU 716447 B AU 5111798 A EP 0944303 A ZA 9710961 A	24-02-2000 29-06-1998 29-09-1999 07-06-1999
US 3639262 A	01-02-1972	NONE	
EP 0862857 A	09-09-1998	AU 5640798 A BR 9800847 A CA 2230769 A JP 2891983 B JP 10291903 A NZ 329894 A	10-09-1998 02-05-2000 06-09-1998 17-05-1999 04-11-1998 28-10-1999
WO 9705779 A	20-02-1997	FR 2737390 A AU 701405 B AU 6744496 A BR 9610078 A CA 2225546 A CN 1193888 A EP 0869713 A JP 11510504 T NZ 315688 A US 5958439 A	07-02-1997 28-01-1999 05-03-1997 02-03-1999 20-02-1997 23-09-1998 14-10-1998 14-09-1999 30-08-1999 28-09-1999
EP 0489322 A	10-06-1992	DE 4038913 A CA 2057137 A US 5213585 A	11-06-1992 07-06-1992 25-05-1993
US 3309182 A	14-03-1967	NONE	
EP 0472310 A	26-02-1992	AT 146337 T AU 653351 B AU 8171891 A BR 9103431 A CA 2047968 A DE 69123661 D DE 69123661 T DK 472310 T EP 0672346 A ES 2095916 T ES 2079336 T GR 3022787 T JP 4265141 A MX 9100612 A NZ 239306 A US 6121199 A US 6121200 A US 5703015 A US 5683958 A US 6063733 A ZA 9106302 A	15-01-1997 29-09-1994 13-02-1992 19-05-1992 10-02-1992 30-01-1997 28-05-1997 09-06-1997 20-09-1995 01-03-1997 16-01-1996 30-06-1997 21-09-1992 01-04-1992 27-04-1994 19-09-2000 19-09-2000 30-12-1997 04-11-1997 16-05-2000 26-08-1992
US 5902772 A	11-05-1999	US 5763495 A AU 6281598 A EP 0888283 A WO 9814422 A ZA 9708724 A	09-06-1998 24-04-1998 07-01-1999 09-04-1998 01-07-1998

INTERNATIONAL SEARCH REPORT

information on patent family members

Interr. Application No

PCT/US 00/22542

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4019362 A	03-01-1991	FR 2648316 A	21-12-1990
		AU 5756590 A	03-01-1991
		BR 9002986 A	20-08-1991
		CA 2019087 A	20-12-1990
		DK 149390 A	21-12-1990
		GB 2233229 A, B	09-01-1991
		GR 90100459 A	15-11-1991
		HU 54023 A	28-01-1991
		IT 1248734 B	26-01-1995
		JP 3034901 A	14-02-1991
		LU 87747 A	18-02-1991
		NL 9001407 A	16-01-1991
		PT 94414 A	08-02-1991
		SE 9002166 A	21-12-1990
		ZA 9004785 A	24-04-1991